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14. ABSTRACT
Scanning Probe Microscope (SPM), and Nanoindenter system equipment will allow us to bridge the divide between the fundamentals of materials science, chemistry, physics, biology, nanomanufacturing, and engineering, and it serves as a unique training platform for students from science and engineering. Such combined system integration permits correlation of SPM topography of a sample surface with micro Raman spectra, and it enables the characterization of local mechanical, chemical and electrical properties in-situ and simultaneously in active polymers and nanocomposites.

Due to the custom-built nature of the equipment and the fact,that receipt of the DURIP funds were delayed, the equipment was finally delivered on January 2009. Installation took place within a month, and was completed by end of February 2009. Two researchers in PI Ounaies' group were trained on most of the functions. So far, the focus has been on getting familiar with the SPM, nanoindentation and Raman spectroscopy functions. In the next few months, the focus will shift to the unique features such as the combined Raman and nanoindentation and the SPM/Raman combinati

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Supplement to Final Report

ACQUISITION OF A COMBINED MECHANO-ELECTRO-CHEMICAL CHARACTERIZATION EQUIPMENT FOR ADVANCED NANOCOMPOSITES RESEARCH AND EDUCATION

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Program manager: Dr. Les Lee

Program: Mechanics of Multifunctional Materials and Microsystems

Contract/Grant #: FA9550-07-1-0558

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ABSTRACT

We have acquired a custom-designed Nanonics Multiview 400 Combined microRaman, Scanning Probe Microscope (SPM), and Nanoindenter system. Such combined system integration permits correlation of SPM topography of a sample surface with microRaman spectra. The Nanonics SPM/NSOM component generates surface morphology images while Raman components can measure electrical properties and chemical signatures. The presence of the Nanoindenter allows simultaneous detection of Raman peaks under stress. The broad goal is to permit characterization of local mechanical, chemical and electrical properties *in-situ and simultaneously* in active polymers and nanocomposites. The proposed equipment will greatly impact an ongoing AFOSR project on active nanocomposites, as well as ongoing and proposed DoD and NSF projects lead by the PIs. The capabilities of the custom-designed Nanonics expand to nanoscale mechanical, electrical, and chemical properties of metallic and ceramic thin films and coatings, and MEMS and NEMS devices, extending its impact to a variety of ongoing and future collaborations and research projects. The combination of micron-scale and nano-scale techniques in the proposed equipment makes it uniquely capable of bridging the gap between interfacial interactions and macroscale properties in advanced materials in general and nanostructured materials in particular. The surface morphological information, internal stress, and electrical properties of such materials have been studied separately and the structure-property is yet to be related intrinsically. Having such a system will enable us to investigate the interfacial forces between components and understand the effects of molecular structure and inclusion distribution on nanocomposites. The simultaneous capabilities of the custom-designed equipment are unique and will complement and expand our research and current materials characterization infrastructure, specifically in the area of multifunctional materials.

Due to the custom-built nature of the equipment and the fact that receipt of the DURIP funds were delayed, the equipment was finally shipped to our laboratory in January 2009. The complexity of the equipment required that an engineer from Nanonics travels to our laboratory to install it and train users. By end of February, the equipment was operational and two researchers were trained on most of its functions. The following months, the focus was on testing and getting familiar with each of the three operations: The Scanning probe microscope, the nanoindentation, and the Raman spectroscopy. In the next step, presently and for the next month, the researchers are training on using the unique features such as the combined Raman and nanoindentation, and SPM and Raman.

Contents

I. Reason for Submitting this Supplement

Due to the custom-built nature of the equipment and the fact that the DURIP finds were delayed almost a year, when the equipment was finally shipped to our laboratory (January 2009) and installed (end of February 2009), the final report was due. Therefore, the final report only contained information on limited use of the equipment by then. I am submitting this supplemental report to describe the advances we have made on using the equipment since its installation.

II. Goals of Using the Equipment

The acquisition of the custom-designed Nanonics Multiview 400 Combined microRaman, Scanning Probe Microscope (SPM), and Nanoindenter system equipment has allowed us to bridge the divide between the fundamentals of materials science, chemistry, physics, biology, nanomanufacturing, and engineering, and it serves as a unique training platform for students from science and engineering. Such combined system integration permits correlation of SPM topography of a sample surface with microRaman spectra, and it enables the characterization of local mechanical, chemical and electrical properties *in-situ and simultaneously* in active polymers and nanocomposites.

In particular, there are several advantages of using this system:

- Simultaneous and on-line data collection from both nanoindentation/scratch and microRaman modalities. This enables the direct intensity comparisons in Raman images for chemical, phase, and stress analysis.
- Direct and extremely localized observation through the optical fibers within the SPM and Raman tip (lens).
- Direct measurement and comparison of localized stress and phase transformation.

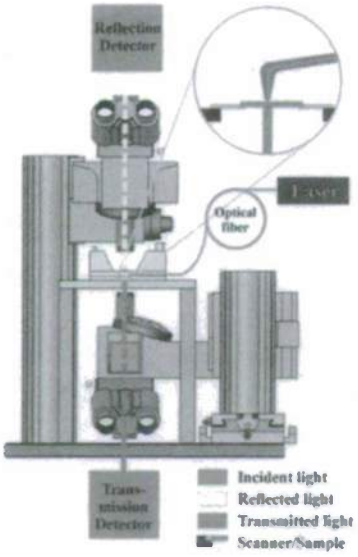
III. Detailed Description of DURIP Equipment

The equipment combines nanoindentation and nanoscratch with scanning imaging analysis:

- The SPM images and measures surfaces on a nanometer length scale within a few layers of atoms. With a sharp tip, (range of 3-50 nm radius of curvature), interactions between the tip and material surfaces can be precisely detected. See Figure 1.

Figure 1. A SPM/NSOM/Confocal system attached to a spectral imaging system. (SPM, Nanonics Imaging Ltd.). This system is configured with nanoindentation and scratch capability. (Nanonics)

- To further customize the equipment to our needs, the Nanonics MultiView 400™ system is directly integrated into the Renishaw RM Series Raman Microscope together, as illustrated in Figure 2. These microscopes employ the upright microscope configuration, and the Nanonics MultiView 400™ is readily placed on the sample stage of such a microscope.



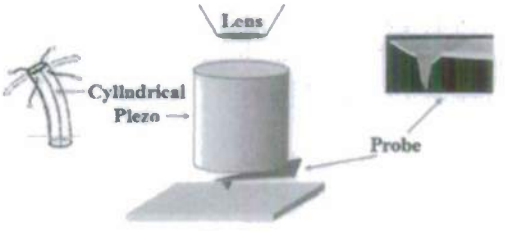


Figure 2, Schematic of the proposed system. (Nanonics)

- The Nano-indentation/SPM system is a unique instrument for characterizing the elastic, plastic, stress-strain, hardness, creep, fracture, residual stresses and other mechanical properties of coatings, thin films, interface, bulk materials and the near surface region of materials.

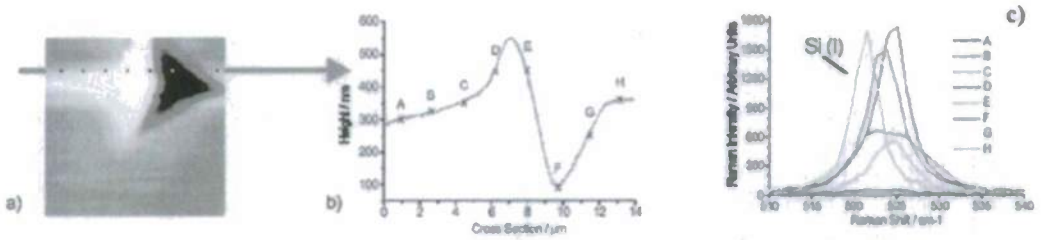


Figure 3. Simultaneous AFM/SPM and Raman on single crystal silicon related to topographical position in a nanoindent:A 14 x 14 micron AFM height image of a nanoindentation in Si is shown here (Figure 3a) with a line scan (b) through a region of this AFM image. The points on the AFM cross section are points at which Raman microscope spectra were collected (c). As a result of the nanoindentation, it can be seen that the silicon has been displaced. The question is whether or not these regions correspond to different phases of the silicon that can be correlated with the AFM measurements. Only Raman microprobe spectroscopy can give this information. The Raman spectra were obtained at the same time as the topography was being measured. ***(http://www.nanonics.co.il/)***

- The microRaman system is capable of measuring spectra from both solid and liquid samples. Using this system, it is possible to investigate crystal structure, orientation, composition and stress. In-situ temperature dependent measurements in polymers and biomaterials can also be carried out. Of particular relevance to our *active nanocomposites* research is the fact that Raman Spectroscopy is sensitive to the radial breathing mode and the tangential mode of carbon nanotubes.

In addition, the equipment is upgradable, where additional capabilities can be attached, such as high vacuum and cryogenic environmental chamber, to allow the direct study of surface chemistry and thermal properties with a nanoindenter for example.

The equipment was delivered on January 2009. Installation took place within a month, and was complete by end of February 2009. Training can take up to a year, so we are continuing to get familiar with all of the unique capabilities of the equipment.

IV. DURIP Equipment-Enabled Research

The equipment is greatly impacting an ongoing AFOSR project, namely AFOSRGrant No. FA9550-06-1-0422 (Title: Active Nanocomposites: Energy Harvesting and Stress Generation Media for Future Multifunctional Aerospace Structures, PI: Z. Ounaies; Program Manager: Dr. Les Lee/Mechanics of Multifunctional Materials and Microsystems) and a newly awarded AFOSR project (Title: Electromagnetically Tunable Fluids, Start date: 1-JUL-2008, PI: D. Lagoudas, Co-PIs: Z. Ounaies and Greg Huff).

Mechanical reliability is an important factor in designing as well as characterizing multifunctional materials. Different characterization techniques are used to investigate mechanical integrity of the structure under load. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are the most common methods to investigate fracture mechanism as well as crack propagation in addition to other microscopic phenomena at region of

failure. However, microscopy techniques usually need extensive sample preparation procedures. They also cannot provide quantitative analysis of fracture mechanism in the sample. There is a great need for a more quantitative study of materials behavior under load.

A. Nano-indentation

Nano-indentation is a relatively new mechanical characterization technique that has been shown to be efficient in studying materials' mechanical behavior at the nanoscale. Nano-indentation can be considered as a nano hardness test. A nano-indentor (Figure 4) applies plastic deformation on the surface of a sample by applying a force. The height of penetration is monitored as well as the amount of force applied to the sample. The results of the test would be a force-height diagram which can be converted to mechanical properties of the sample like elastic modulus and hardness (Figure 5). One of the advantages of nano-indentation is the ability to apply nanoscale deformation on the sample. Nano-indentation increases the accuracy to apply local deformation at the nanoscale and detect the in-situ behaviour of nanocomposites in different regions of the material. Lee et. al. investigated mechanical properties of a cellulose fiber reinforced polymer nanocomposite by doing an array of nanoindentation in different regions of the sample. They showed how mechanical properties of different regions in the sample can be differentiated by aid of nanoindentation. Figure 6 shows a schematic view of their experiment. By accurate positioning of the nano-indentor, starting from the fiber area, moving to the interphase and finally reaching the matrix, they were able to measure Hardness as well as Modulus values of the fiber and polymer as well as those of the interphase region (Figure 26).

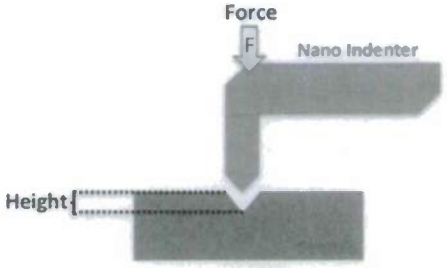


Figure 4. A schematic view of Nano-indentation test

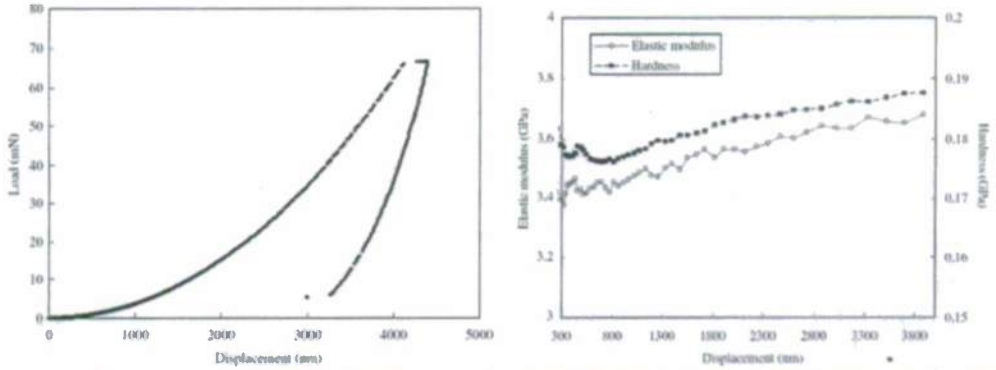


Figure 5. (left) Load (mN) (right) Elastic modulus and Hardness versus Displacement result of a nanoindentation test.

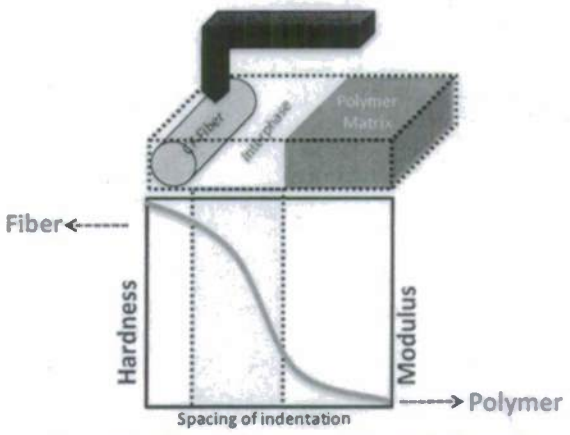


Figure 6. An schematic view of Lee et. al. Nanoindentation experiment

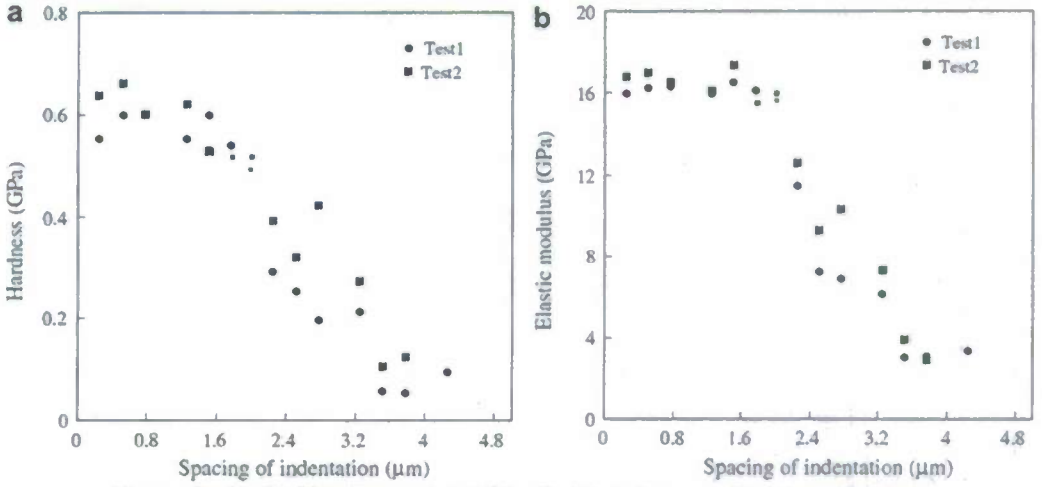


Figure 7- (Left) Hardness (right) Elastic Modulus as a function distance

B. Raman spectroscopy

Raman spectroscopy is one of the most powerful spectroscopy techniques to characterize various properties of CNTs and CNT based polymer nanocomposites. The non-invasive nature of Raman experiment as well as convenience usage and the ability to be combined with other techniques makes it a very useful characterization technique in CNT based polymer nanocomposites. In Raman spectroscopy, a sample is illuminated by a light source of single frequency and the scattered light is collected by an optical sensor. The difference between the energy of the incident light and the scattered light is the energy difference between the ground state and the excited state of the molecule and is plotted as the intensity versus Raman shift (wavenumber) of the sample (Figure 8).

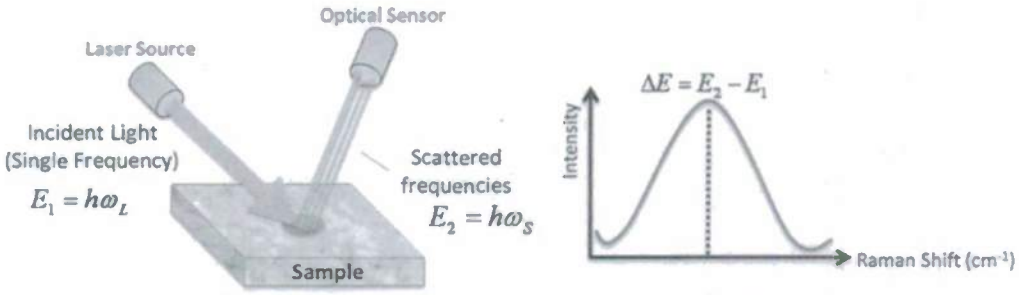


Figure 8- Raman Spectroscopy (A schematic view)

C. In-situ Raman combined with mechanical tests

Raman speetroseopy has been eombined with other teehniques to investigate Raman behavior of CNTs under applied meehanical deformations. Swan et. al. used atomic force mieroscopy (AFM) and stretched a single wall carbon nanotube (SWNT) by aid of an AFM tip. In the meanwhile they took Raman spectrum of the stretched SWNT by focusing Raman laser on it.

As can be seen in the Figure 9, after stretehing SWNT, Raman peaks shift to lower wavenumbers. By this study, Swan et. al. were able to prove that Raman speetrum of CNTs is sensitive to meehanieal deformation and this meehanieal deformation, here CNTs elongation, ean be eharaeterized by Raman spectroscopy.

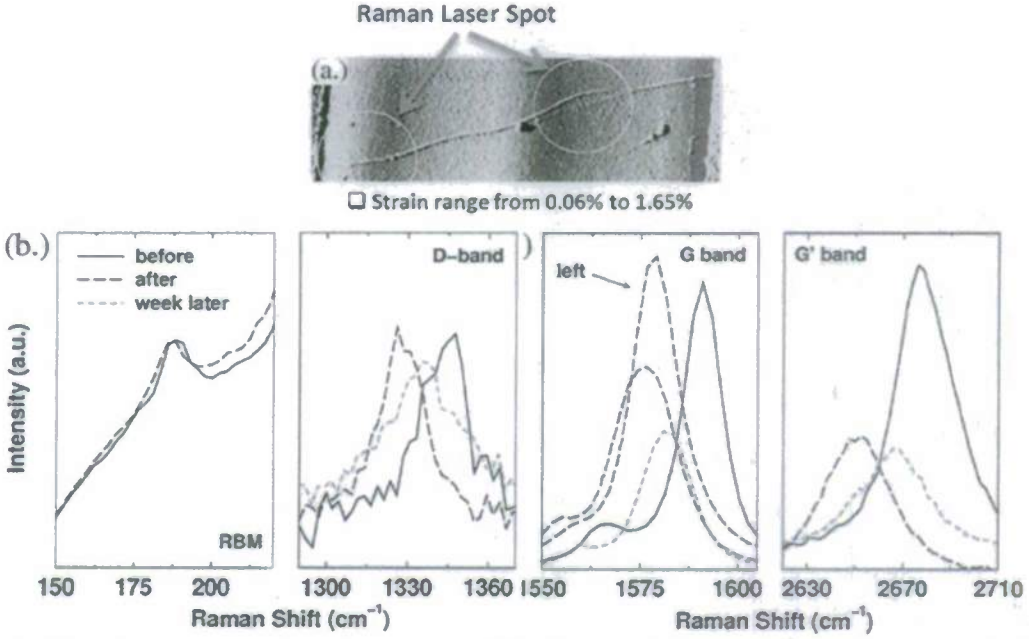


Figure 9. (Top) Raman Laser spot on stretched SWNT by AFM (Bottom) Raman Spectrum of SWNT before and after stretching by AFM tip.

D. In-situ Raman spectroscopy/nano-indentation experiments

In this study we proposed the idea of combining Raman spectroscopy and Nano-Indentation with the aim of characterizing mechanical deformation of the CNT/PVDF nanocomposite. Figure 10 shows three different scenarios that might happen when a CNT/PVDF sample is nanoindented.

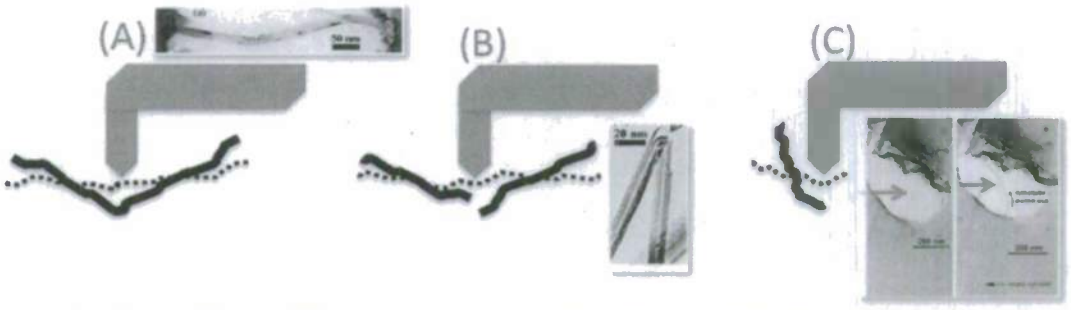


Figure 10. Three different failure mechanism scenarios of Raman Spectroscopy/Nano-Indentation experiment (A) Elastic deformation of CNT inside matrix (B) Breaking CNT in the matrix and (C) CNT pull out from the matrix

In the first scenario (A), elastic deformation of the CNT in the matrix is considered. In this case, CNT is either stretched, compressed or bent under Nanoindetation test. It is expected that a Raman shift would be observed upon nanoindentation. In the second scenario (B), Nanoindentation is beyond the elongation at break of the CNTs and causes CNTs to break under load. In this case, a Raman shift should be observed before breaking the CNTs. But promptly after CNTs break, Raman shift should return to its original position. In the last scenario (C), CNTs would be pulled out from the matrix. In this case interphacial bonding between CNTs and the PVDF is not strong and Nano-indentation simply separates the CNTs from the matrix. In this case, no Raman shift is expected to be observed.

E. Experimental procedure

Figure 11 schematically shows the experimental setup of in-situ Raman/Nano-Indentation experiment used in this study. The experiment was done in three major steps:

Step 1- Raman Spectroscopy of the sample
Step 2- In-situ Raman while Nano-indenting the sample
Step 3- Raman Spectroscopy of the indented area after Indentation

Nanoindentation was done in different indentation depths from 40 to 200nm in 40nm increments.

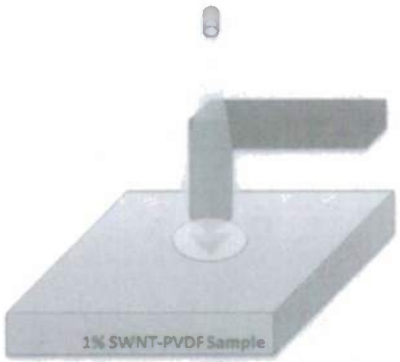


Figure 11. A schematic view of the in-situ Raman/Nano-indentation setup

F. Results and discussion

Raman Spectrum of SWNT in bulk besides SWNT embedded in PVDF are shown in Figure 31. As it seen in the Figure 12, the is an increase in wavenumber of all three major CNT bands after embedding in PVDF. This increase in Raman shift is a good sign of interaction and interfacial strength between SWNTs and PVDF polymer.

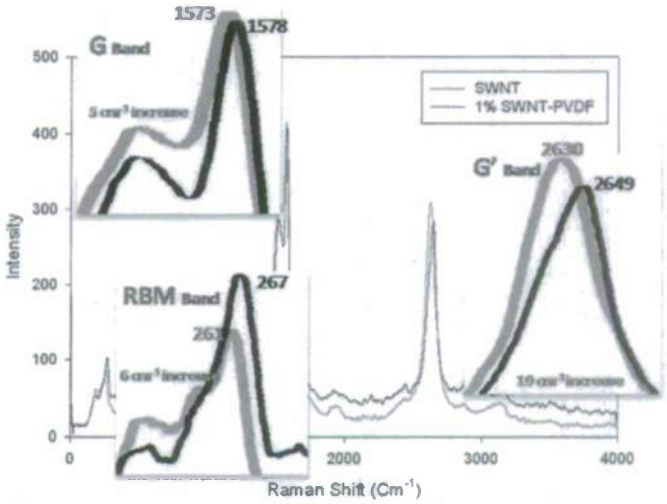


Figure 12. Raman Spectroscopy, SWNTsand SWNT-PVDF Nanococomposite

Figure 13 shows in-situ Raman/Nano-Indentation results in 120nm indentation depth. RBM and G-band didn't show any sensitivity to Nano-indentation. However G' band showed increase in Raman shift of the SWNTs after doing Nanoindetation.

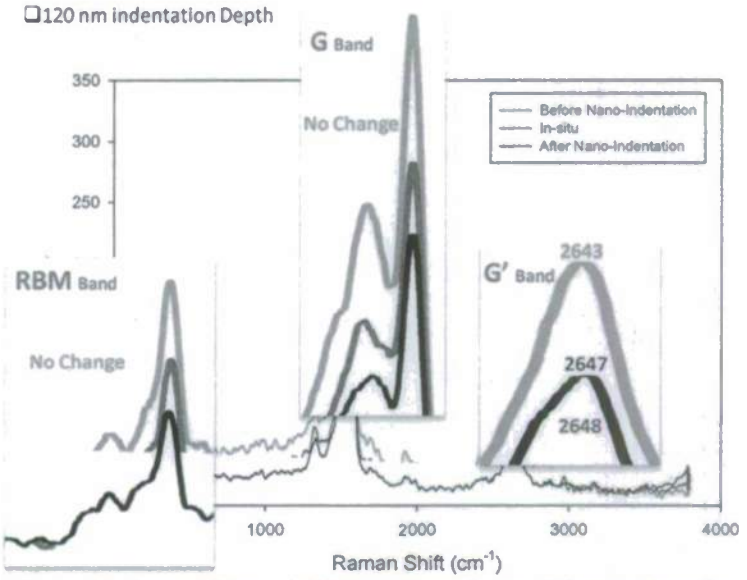


Figure 13. In-situ Raman/Nano-indentation results in 120nm indentation depth

Our results are also presented in Figure 14 for the Raman shift change as a function of indentation depth. It can be seen that there is an increasing trend by going to higher indentation depths. The highest Raman shift was observed in 120nm which can be a sign of highest indentation depths. After 120nm the Raman shift started decreasing. It can be argued that in indentations higher than 120nm, SWNTs undergo beyond deformation at break and cannot hold any more deformation. This causes SWNTs to break and as a result a decrease in Raman shift is observed.

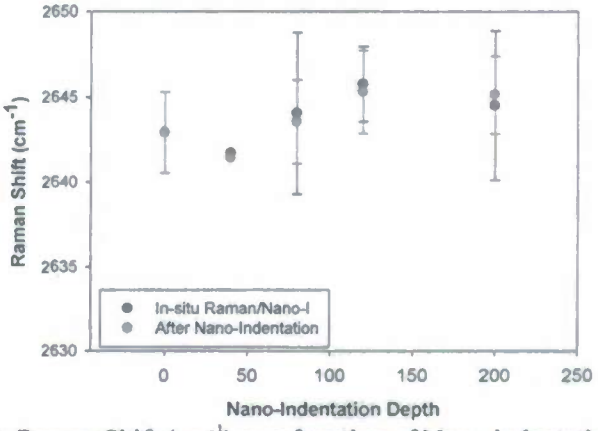


Figure 14. Raman Shift (cm^{-1}) as a function of Nano-indentation depth